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CHARACTERIZATION OF DEFECT GROWTH STRUCTURES IN ION PLATED FILMS BY SCANNING ELECTRON MICROSCOPY

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INTRODUCTION

Adherence and homogeneous growth morphology of a coating is of paramount importance for any engineering application. The growth morphology and the resultant properties of ion plated coatings are interrelated and controlled by the substrate condition and the ion plating parameters. Ion plated films have demonstrated the strongest adherence, not achieved by the other deposition methods (refs. 1 and 2). However, one difficulty normally arises, the inability to produce homogeneous, defect-free or pore-free films over large surface areas. When coatings are ion plated on surfaces, it is practically impossible to prepare surfaces which are atomically smooth over an appreciable area. Surface microdefects are inherent to polycrystalline metals and cannot be completely eliminated. Consequently, homogeneous morphological growth during ion plating is very difficult to obtain. Therefore, it is not only important to understand the coating-matrix morphology, which is always related to a smooth deposition and growth, but it is also important to identify the morphological growth of the defect.

Defect growth has been observed and reported in coatings deposited by electroplating (ref. 3), electroless plating (ref. 4), thermal evaporation (ref. 5), and sputtering (ref. 6). These defect structures have adverse affects on the coating. They act like stress raisers, therefore weakening the mechanical properties of the coating by creating porosity and introducing cracks. Substrate defect-induced nucleation and growth are of great practical importance in coatings used for tribological and corrosion applications. Friction and wear behavior is sensitive to

surface topographical characteristics, especially where surfaces are subjected to small oscillatory slip under load. It is of interest not only to identify and understand the factors that create and control defect formation in a coating, but also to learn how to suppress or eliminate it. Presently there are no studies reported in the literature on defect growth in ion-plated films. The objective of this investigation was to identify and classify these defects as to their geometrical appearance by scanning electron microscopy (SEM) and to trace the particular cause or origin of their formation.

APPARATUS AND PROCEDURE

The ion-plating chamber used in this study has been previously described (ref. 7). The plating conditions used are those most commonly encountered in commercial ion plating. A negative potential of 3 to 5 kV was applied to the specimen, with a substrate current density of 0.3 to 0.8 mA/cm^2 in argon at a pressure of 20 millitorr. The specimen to boat distance was 10 cm. Before evaporation, the substrates were dc-sputter cleaned for 10 minutes.

The substrates were 1.25 cm-diameter, 304-stainless-steel disks. Before ion plating the disk specimens were finish ground on 600-grit emergy paper, then polished with 3-μm diamond paste, and finally rinsed with acetone and absolute ethyl alcohol. The surface roughness of the steel disks was less than 2×10^{-2} μm. For ion plating the disks were mounted in a circular, stainless-steel holder (6.25 cm in diam and 1.25 cm thick). Gold and copper of 99.99-percent purity were the plating materials, and the coating thickness ranged from 0.2 to 2 μm. The bulk temperature was monitored by a Chromel-Alumel thermocouple embedded in the holder and maintained at 125° C. For comparison of surface roughnesses, several mica and microscope-glass slides were also ion plated. The surface morphology of the deposited coatings was examined by SEM.

RESULTS AND DISCUSSION

During ion plating, coating defect growth is basically dominated by the substrate topography. The most common causes are surface roughness (finish), particulate

contamination of the surface, intercrystalline growth between growing crystals, and actual deposition conditions (evaporation rate, plasma instabilities, etc.). Substrate defect induced nucleation is of great engineering importance, since most practical substrates contain a range of preferential nucleation sites of varying potencies. As the coating thickness increases beyond 1 μm, the size of the growth defects also increases and exerts increasing internal stresses in the coating. From SEM observations, three distinct types of coating growth defects can be distinguished: (1) nodular growth, (2) abnormal or runaway growth, and (3) spits. An attempt is made to trace these three defect types to the causes or origin of their formation.

NODULAR GROWTH

Nodules are coating defects that are basically nucleated by substrate defects, such as surface irregularities, microscratches, slip lines, inclusions, and impurities; and also form as a result of coating growth disorders that occur during the plating process. These defects generally have two distinct appearances: the typical nodular or conical growth with a dome or egg-shaped top that projects above the coating-matrix surface, and the reverse nodular growth with a hole formation in the center resembling a crater. A typical nodular construction is shown in figure 1. The surface of the nodule is a circular arc, and it projects above the substrate by a distance h. The diameter of the nodule d increases as the coating thickness t increases. The boundary of the nodule is parabolic in shape, which indicates an ever-increasing size with continuing deposition. As a result, the nodules tend to grow in size with increasing coating thickness.

Nodules can grow individually as shown in figure 2(a) or grow together or overlap to form compound aggregates. The exact configuration and dimensions of a nodule, whether it is an individual or an aggregate, depend on the size and spatial distribution of the nucleation sites. The size of the individual nodules varies from less than 1 micrometer to several micrometers in diameter. The aggregate structures can, however, be over tens of micrometers in length.

The substrate defect nucleation sites are the points with high energy concentration for preferential nucleation and growth (ref. 8). Therefore, accelerated growth occurs at these sites relative to the matrix growth and a distinct disregistry, or separation, forms between the defect structure and the matrix. These separations are the weakest areas in the coating, and the coating tends to break around the nodule edges. As a result, the nodule may simply be ejected from its place and leave a cavity. Such a displaced nodule with a cavity is shown in figure 2(a).

A high concentration of these cavities creates porosity and weakens the coating structure. It should be recognized that the diameters of the nodules and therefore the diameters of the cavities increase as the coating thickness increases (fig. 2(a)). Films about 1 micrometer thick may have a nodular diameter, and consequently a cavity diameter, as large as several tens of micrometers in size.

A typical nodular growth does not significantly change its profile with film growth from the parabolic shape which suggests that the growth rate is surface controlled. Preliminary results with nickel substrates having (100) and (111) orientations indicate that substrate orientation does not effect the orientation in copper nodules, as their orientations varied from that of the substrate.

Another defect structure of the nodular type looks like a crater, with a hollow central section and displaced material forming the walls as shown in figure 2(b). The crater formation may be considered as reverse nodular growth. Instead of a circular arc that extends above the coating-matrix surface, a circular crater is formed, the walls of which extend above the coating-matrix surface. The cause of crater formation is still unknown, but it may be attributed to a particular type of surface roughness where the substrate asperities have a certain distribution that exerts a repelling effect between the growing crystallites. When very smooth surfaces such as cleaved mica were ion plated, nodular growth and crater formation were not observed.

To obtain additional insight about the microstructure of the matrix and the defects, 304-stainless-steel disks which were ion plated with copper were polished with diamond paste and subsequently etched with 5-percent nital. Microscopic examination reveals that the areas around the craters, which constituted the area of the displaces material, showed a nonuniform appearance due to surface roughening (ref. 7). Evidently, the coating defect areas around the craters have different etching rates than the adjacent coating matrix.

These coatings were also exposed to such mechanical forces as rubbing and sliding to determine the behavior of the nodules under these conditions (ref. 7). The copper-plated, 304 stainless-steel disks were unidirectionally rubbed on plain bond paper impregnated with diamond polishing paste. After rubbing, the larger nodules are pulled out, leaving vacancies, and the small nodules are left intact. When a nodule reaches a certain diameter on the coating surface, it will tend to break around the edges and be pulled out especially under imposed mechanical forces.

ABNORMAL OR RUNAWAY GROWTH

Abnormal or runaway crystallographic growth defects generally have very unusual, nonsymmetrical features of a runaway (lateral or vertical) growth as shown in figure 3. The cause of these features is predominantly due to external sources such as nonmetallic particles or other foreign matter loosely held on the surface or embedded from mechanical polishing. These stray particles or contaminants act as the initial preferential high points, and accelerated growth occurs rapidly. This accelerated, nonsymmetrical growth pattern, which results in significant, irregular changes in surface profile, is believed to be primarily controlled by gas-phase diffusion (ref. 9). If the rate was strictly surface controlled, as nodular growth, there would be no significant changes in the surface profile of the runaway defects. Extended runaway defects are very loosely bonded in the coating matrix, break off easily, and exhibit a different type of defect-matrix interface than nodules.

Spits

Spits, or "spats," are crystallographic defects that are formed during ion plating and that have an entirely different origin than the other defect types. Spits are caused by nonuniform or very fast evaporation of the molten vapor source. This generally occurs by spontaneous eruption of the evaporant through the skin as a result of either rapid expansion of adsorbed gases in the molten charge or uneven temperature distribution when the evaporant temperature is rapidly raised. In both instances, small droplets are ejected from the molten vapor source, land on the surface in a molten state, and are incorporated into the coating as shown in figure 4. Spits can be easily distinguished from the other defects since they always have a typical circular shape and may have a partial circular depression in the center. Spits can be totally eliminated by imposing strict evaporation controls to obtain uniform evaporation rate.

SUMMARY OF RESULTS

Gold and copper films (0.2 to 2 μm thick) were ion plated on very smooth 304-stainless-steel and mica surfaces and examined by scanning electron microscopy for defect morphological growth. The following results were obtained:

1. Three types of coating defects were distinguished: nodular growth, abnormal or runaway growth, and spits.

2. The potential nucleation sites for defect growth were examined to determine the cause of defect formation. Nodular growth is due to inherent surface micro-defects, abnormal or runaway growth is due to external surface inclusions, and spits are due to nonuniform evaporation and ejection of droplets.

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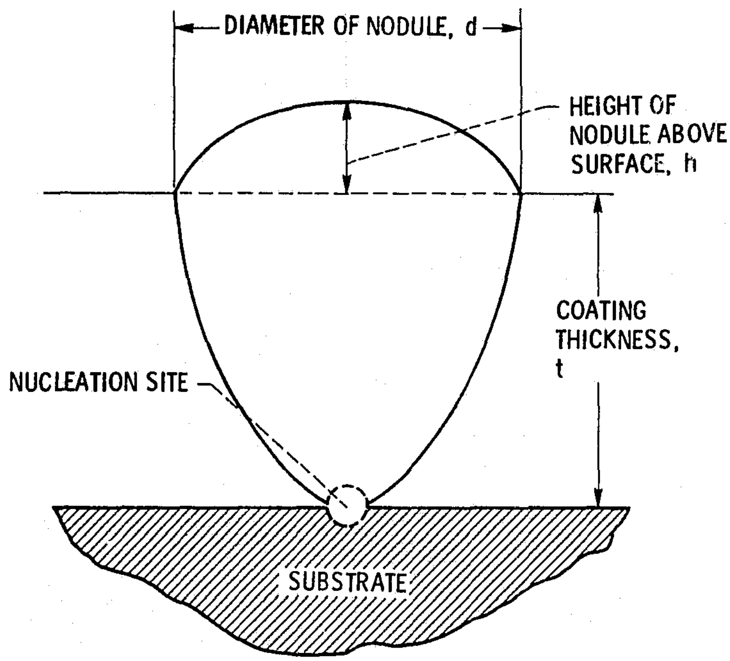
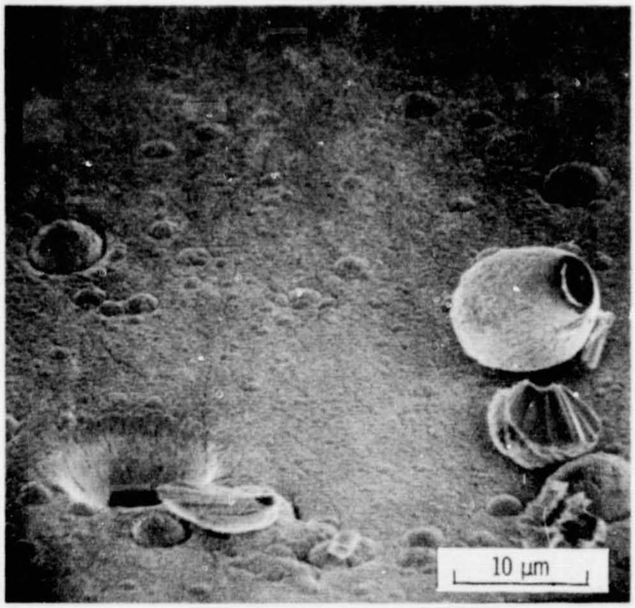
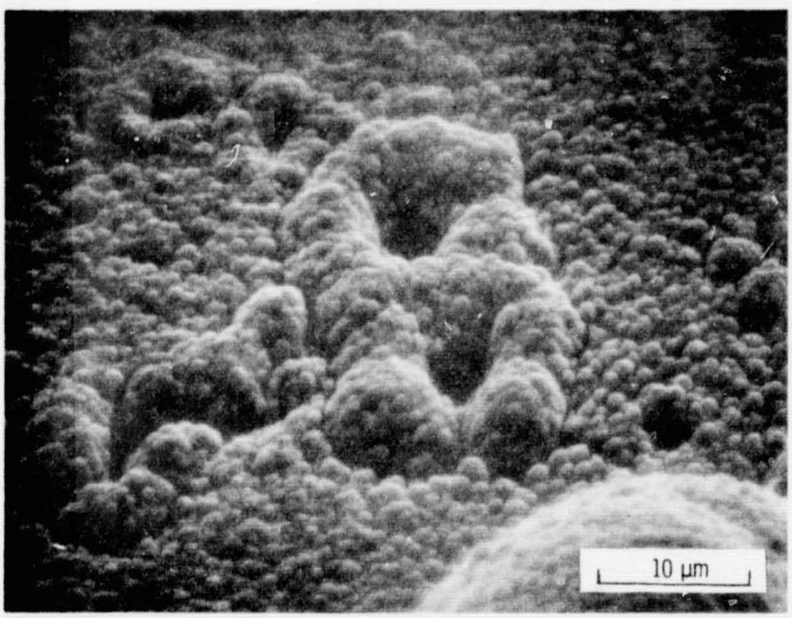


Figure 1. - Geometric construction of typical isolated nodule.



(a). Ejected nodule with a vacancy in ion-plated gold.



(b). Crater formation in ion-plated copper.

Figure 2. - 304 stainless steel subtrates ion-plated with gold and copper.

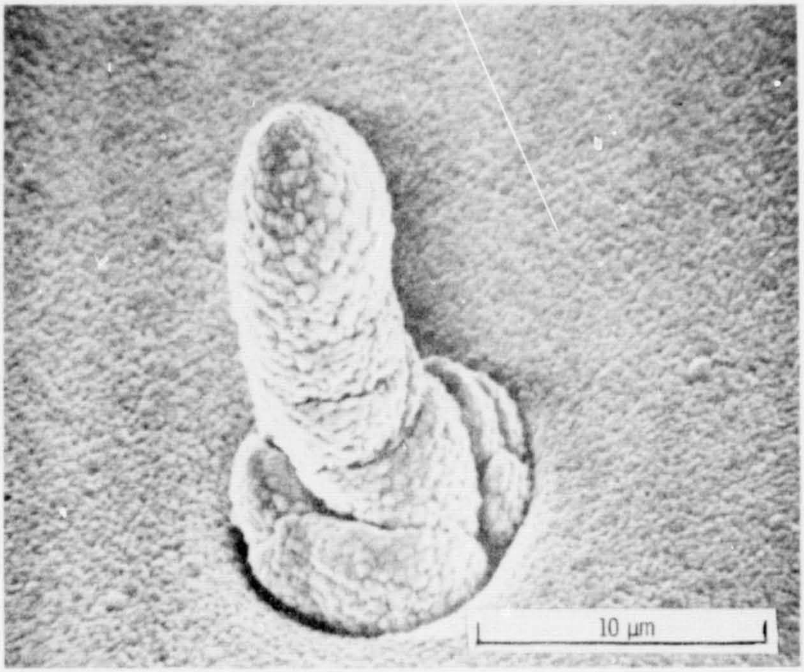


Figure 3. - Abnormal or runaway growth in ion-plated copper on 304-stainless steel.

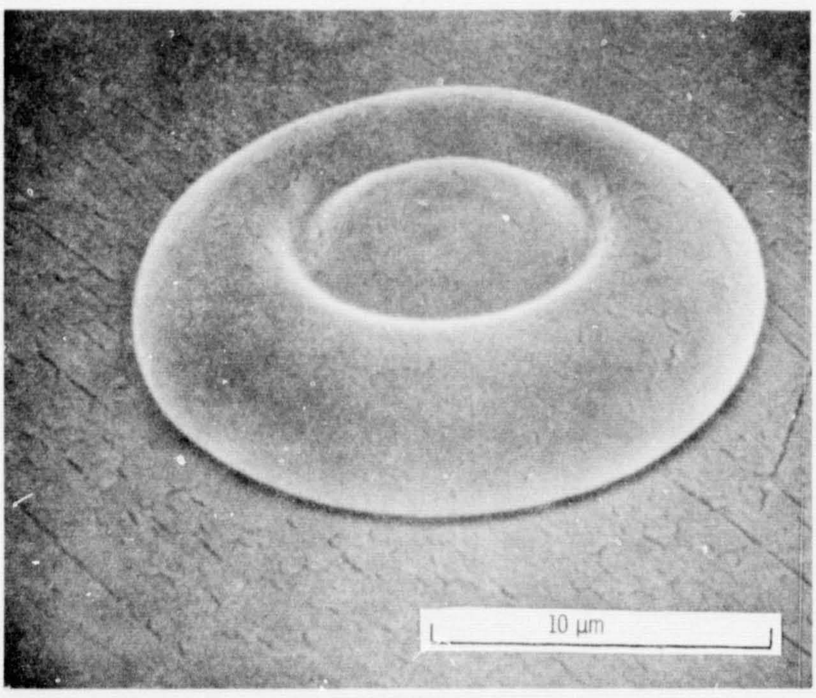


Figure 4. - Spit in ion-plated gold on 304-stainless steel substrate.